

# Band-width control in a perovskite-type $3d^1$ correlated metal $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ . II. Optical spectroscopy investigation.

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Optical conductivity spectra of single crystals of the perovskite-type  $3d^1$  metallic alloy system  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  have been studied to elucidate how the electronic behavior depends on the strength of the electron correlation without changing the nominal number of electrons. The reflectivity measurements were made at room temperature between 0.05 eV and 40 eV. The effective mass deduced by the analysis of the Drude-like contribution to the optical conductivity and the plasma frequency do not show critical enhancement, even though the system is close to the Mott transition. Besides the Drude-like contribution, two anomalous features were observed in the optical conductivity spectra of the intraband transition within the  $3d$  band. These features can be assigned to transitions involving the incoherent and coherent bands near the Fermi level. The large spectral weight redistribution in this system, however, does not involve a large mass enhancement.

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## I. INTRODUCTION

Over the past few decades, a considerable number of studies have been performed on  $3d$  transition-metal oxides which have a considerably narrow  $3d$  band. In particular, a metal-to-insulator transition caused by a strong electron correlation<sup>1</sup> (Mott transition) as well as anomalous electronic properties in the metallic phase near the Mott transition have attracted the interest of many researchers. Since the discovery of the high- $T_c$  cuprate superconductors, the importance of two types of experimental approaches to the Mott transition have been discussed intensively: a filling control and a band-width control. The former consists in doping holes or electrons to the system, and the latter in varying the strength of the electron correlation  $U/W$ , where  $U$  is the electron correlation due to Coulomb repulsion and  $W$  is the one-electron band-width.

In recent years, the systematic evolutions of optical conductivity spectra in going from a correlated metallic phase to the Mott-Hubbard insulating phase have been reported on both the filling controlled<sup>2-6</sup> and the

band-width controlled Mott-Hubbard systems.<sup>7-10</sup> The smallest energy gap for charge excitations of the Mott-Hubbard insulator is the excitation energy of the charge fluctuation  $d^n + d^n \rightarrow d^{n-1} + d^{n+1}$ , so-called a Mott-Hubbard gap.<sup>11</sup> The optical conductivity of the Mott-Hubbard insulator is considered to show a gap feature due to the above charge excitation from the lower Hubbard band to the upper Hubbard band.

$\text{V}_2\text{O}_3$  and related compounds have been extensively studied as typical materials which show the Mott transition with varying the strength of the  $U/W$  ratio. The temperature dependent optical conductivity of  $\text{V}_2\text{O}_3$  was reported by Thomas *et al.* through the metal-to-insulator transition.<sup>9,10</sup> The optical conductivity of  $\text{V}_2\text{O}_3$  in the insulating phase shows a gap feature, which is attributed to the Mott-Hubbard gap excitation. On the other hand, in the metallic state, a low-energy contribution to the optical conductivity shows an anomalous feature, which is reproduced by two Lorentzians. Moreover, the optical conductivity shows an anomalous enhancement of the spectral weight as a function of temperature. Rozenberg *et al.* reported that these experimental results are in good agreement with the theoretical prediction obtained by the

infinite-dimension Hubbard model within the mean-field approach.<sup>10</sup> Since the formation of the Mott-Hubbard bands are predicted even in the metallic state for this kind of strongly correlated system, the optical conductivity spectra should be affected by the precursor features.<sup>12</sup> It is very interesting to see how the spectral weight varies with the electron correlation in the correlated metallic state near the Mott transition. For a detailed discussion, however, we need to control the strength of the electron correlation more precisely.

The perovskite-type early 3d transition-metal oxides are ideal Mott-Hubbard systems for controlling the band filling and band-width by chemical substitutions. It has been reported that, for the filling controlled systems  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$  and  $R_{1-x}\text{Ca}_x\text{TiO}_3$  ( $R$ =rare earth), the spectral weight of the optical conductivity transfers from the higher energy feature corresponding to an excitation through the Mott-Hubbard gap, to the mid-infrared inner-gap region corresponding to the Drude-like absorption extending from  $\omega = 0$ .<sup>2,3,6</sup> The rate of the spectral weight transfer by doping increases systematically with the increase of the one-electron band-width  $W$ .

On the other hand, the Ti–O–Ti bond angle can be decreased as we decrease the ionic radius of the  $R$  site. The decrease of the Ti–O–Ti bond angle gives rise to the decrease of the value of  $W$ . A systematic change of the optical conductivity spectra was reported on  $RT\text{TiO}_3$  ( $R$ =La, Ce, Pr, Nd, Sm, and Gd).<sup>7</sup> The lowest gap-like feature systematically increases as the ionic radius of the  $R$  site decreases, namely, as the value of  $W$  decreases. A similar change was also observed on an alloy system,  $\text{La}_{1-x}\text{Y}_x\text{TiO}_3$ .<sup>8</sup> These systematic variations of the optical conductivity are interpreted as the successive increase of the Mott-Hubbard gap with the increase of the strength of the  $U/W$  ratio. In these materials, however the system remains an insulator even for the least correlated  $\text{LaTiO}_3$ , therefore one cannot study the evolution of the metallic properties under the band-width control in this system.

The purpose of this paper is to clarify the evolution of the optical conductivity spectrum in the metallic phase near the Mott transition, as we control the strength of the electron correlation  $U/W$  without changing the band filling. A perovskite-type 3d<sup>1</sup> vanadate  $\text{CaVO}_3$  is considered to be a strongly correlated metal close to the Mott transition.<sup>13,14</sup> We can control the strength of the  $U/W$  ratio, by chemical substitution of a Sr ion for a Ca ion of the same valence without varying the nominal 3d-electron number per vanadium ion.<sup>15</sup> We report the optical conductivity spectra in this strongly correlated alloy system  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ . The effective mass  $m^*$  estimated from the optical measurements are shown in Sec. IIIB. The evolution of the optical conductivity is discussed in Sec. IIIC.

## II. Experimental

Single crystals of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  ( $x=0, 0.25, 0.5, 1$ ) were grown by a floating-zone method using an infrared image furnace with double halogen lamps. Details on the

preparation of these samples are described in the preceding paper.<sup>14</sup> Since as-grown samples are slightly oxygen deficient, all the samples were annealed in air at 200 °C for 24 hours in order to make the oxygen concentration stoichiometric.<sup>13,16,17</sup>

Raman scattering spectra were measured at room temperature in back-scattering geometry using a triple spectrometer system (Jasco TRS-600) equipped with a charge coupled device (CCD; Photometrics TK512CB) cooled by liquid nitrogen. The samples were excited by the 514.5 nm Ar ion laser line. Polarization of the incident light was taken to be parallel to that of the scattered light.

Optical reflectivity measurements were carried out at room temperature (~300 K) in the energy range between 0.05 eV and 40 eV using a Michelson-type Fourier-transform infrared spectrometer (0.05–0.6 eV), a grating monochromator (0.5–5.6 eV), and a Seya-Namioka-type grating for the synchrotron radiation (5–40 eV) at the beamline BL-11D of Photon Factory, Tsukuba. The surfaces of the samples were mechanically polished with diamond paste for the optical measurements. The absolute reflectivity was determined by referring to the reflectivity of an Al or Ag film which was measured at same optical alignment.

We have calculated a complex dielectric function  $\epsilon(\omega) \equiv \epsilon_1(\omega) + i\epsilon_2(\omega)$  by the Kramers-Kronig (K-K) transformation of the measured reflectivity  $R(\omega)$ , where  $\omega$  is the photon energy. The real part of the complex optical conductivity  $\text{Re}[\tilde{\sigma}(\omega)]$  is related to the imaginary part of the dielectric function  $\epsilon_2(\omega)$  by  $\text{Re}[\tilde{\sigma}(\omega)] = (\omega/4\pi)\epsilon_2(\omega)$ . Since the K-K analysis requires  $R(\omega)$  for  $0 < \omega < \infty$ , two assumptions must be made to extrapolate the observed data beyond the upper and lower bounds of the measurements. In the present study, the reflectivity data were first extrapolated from the lowest measured energy down to  $\omega = 0$  with the Hagen-Rubens formula which is an approximation for  $R(\omega)$  of conventional metals. Then, beyond the highest measured energy, the reflectivity data were extrapolated up to  $\omega \rightarrow \infty$  with an asymptotic function of  $\omega^{-4}$ .

## III. RESULTS AND DISCUSSION

### A. Band-width control due to orthorhombic distortion

Powder x-ray diffraction measurements were carried out to characterize the samples and to determine the lattice constants. In Fig. 1, we present the lattice constants,  $a$ ,  $b$ , and  $c$  against the Sr content  $x$ . The crystal structure of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  belongs to the perovskite-type structure with orthorhombic distortion ( $\text{GdFeO}_3$ -type).<sup>18</sup> The amount of the distortion is almost proportional to the amount of the Ca content; *i.e.*,  $\text{SrVO}_3$  is a cubic perovskite. However, we assumed the crystal structure of all samples ( $0 \leq x \leq 1$ ) orthorhombic and deduced the lattice constants. The lattice constants increase monotonously with the increase of  $x$ , ensuring the

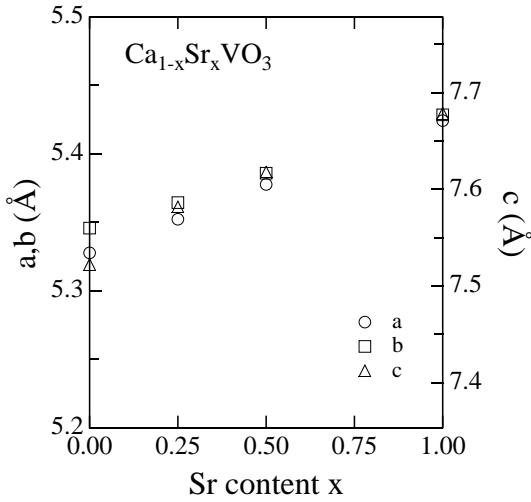


FIG. 1. Lattice constants,  $a$ ,  $b$ , and  $c$  of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  single crystals plotted against the Sr content  $x$ . The data were estimated from powder x-ray diffraction patterns.

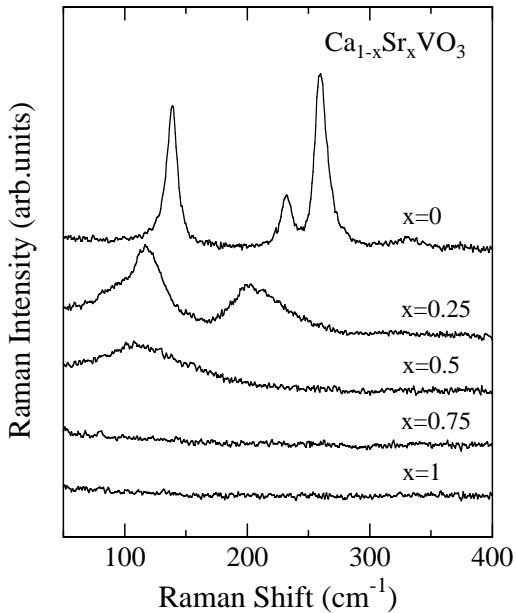


FIG. 2. Raman spectra of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  at room temperature. Polarization of the incident light was taken to be parallel to that of the scattered light.

appropriate formation of the solid solution over the whole composition range.

Raman scattering measurements give indirect information about the crystal symmetry, because the appearance of some Raman-active phonon lines depends crucially on the crystal symmetry of the system. In Fig. 2, we show the Raman spectra of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  at room temperature in the wave-number range of  $80\text{--}400\text{cm}^{-1}$ . In this wave-number range, four Raman active  $A_g$  phonon lines are observed in orthorhombic  $\text{CaVO}_3$  ( $x = 0$ ). The energies of the phonon lines shift to the lower energy side, and the width of the peaks become broader, as we increase the Sr content  $x$ . The Raman active phonon lines disappear completely in  $\text{SrVO}_3$ .

According to the group theory analysis,<sup>19</sup> it is predicted that several Raman active phonon modes  $7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$  can exist in the orthorhombically distorted perovskite which belongs to the point group symmetry of  $D_{2h}$ . On the other hand, the cubic perovskite which belongs to the point group symmetry of  $O_h$  is “Raman forbidden”, namely it has no Raman-active phonon modes. Therefore, the experimental results tell us that the crystal symmetry actually changes from the orthorhombic distorted perovskite ( $\text{CaVO}_3$ ) to the cubic perovskite ( $\text{SrVO}_3$ ). The orthorhombic to cubic transition is considered to occur between  $x = 0.5$  and  $0.75$ .

As discussed in the preceding paper,<sup>14</sup> the orthorhombic distortion implies that the V–O–V bond angle is deviated from  $180^\circ$ , *i.e.*, there is an alternately tilting network of the  $\text{VO}_6$  octahedra. The V–O–V bond angle of  $\text{SrVO}_3$  is  $180^\circ$  same as an ideal perovskite structure, while that of  $\text{CaVO}_3$  is  $\sim 160^\circ$ . The bond angle deviation from  $180^\circ$  reduces the overlap between the neighboring V  $3d$  orbital mediated by the O  $2p$  orbital. Therefore, the one-electron band-width  $W$  of V  $3d$  band decreases with decreasing the V–O–V bond angle. Accordingly, we can control the value of  $W$  by chemical substitution of the  $\text{Ca}^{2+}$  ion for the  $\text{Sr}^{2+}$  ion of the same valence without varying the nominal  $3d$ -electron number per vanadium ion. Since the electron correlation energy  $U$  are almost the same in  $\text{CaVO}_3$  and  $\text{SrVO}_3$ , we can thus control the strength of the  $U/W$  ratio by the chemical substitution. The V–O–V bond angle of  $\text{CaVO}_3$ , in addition, is almost equal to that of  $\text{LaTiO}_3$  which is a Mott-Hubbard type insulator, so that it seems reasonable to consider that  $\text{CaVO}_3$  is close to the Mott transition. Moreover, there are many other evidences of the strong electron correlation in this system discussed so far.<sup>13–17</sup> Thus,  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system is ideal for the study of the metallic states near the Mott transition.

## B. Effective mass

In Fig. 3, we show optical reflectivity spectra of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  measured at room temperature ( $\sim 300$  K), for four single crystals with different  $x$  ( $x = 0, 0.25, 0.50, 1$ ). The chemical substitution of  $\text{Sr}^{2+}$  for  $\text{Ca}^{2+}$  seems to make no remarkable change at the lower-energy region (below  $\sim 5$  eV) in the optical reflectivity spectra. All the samples exhibit high reflectivity from far-infrared to near-infrared region, and we can recognize a sharp reflectivity edge appearing at  $\sim 1.3$  eV. Since  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  is metallic over the whole composition range, the optical reflectivity is dominated by the signal of conduction electrons in this photon energy region. Systematic spectral changes with  $x$  are observed in the energy range of the ultra-violet and vacuum-ultra-violet light. The changes are partly due to the differences in the conduction bands of the  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  cations. But this is irrelevant for the discussion of the main subject.

First of all, we will concentrate on the low energy response of the itinerant carriers. The contribution of the conduction electrons to the complex dielectric function

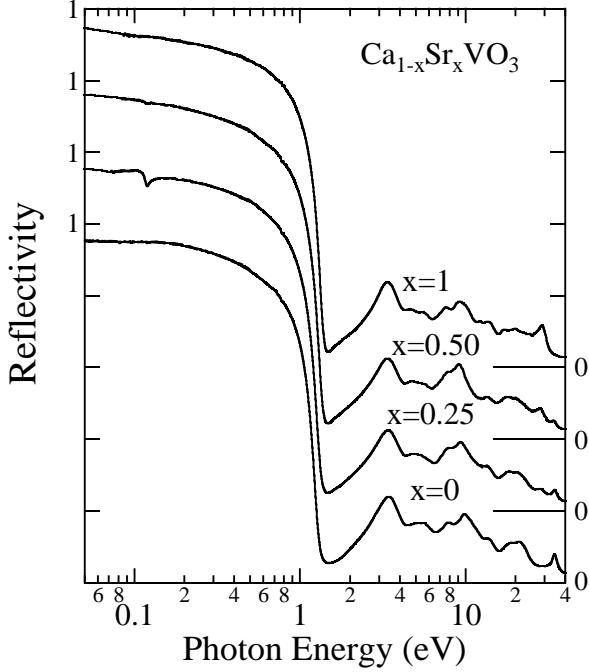


FIG. 3. Reflectivity spectra for the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  single crystals measured at room temperature. The feature at  $\sim 0.1$  eV for  $x = 0.25$  is an experimental artifact.

$\epsilon(\omega)$  is well described by the Drude model. According to the generalized Drude model,<sup>20,21</sup>  $\epsilon(\omega)$  is expressed as

$$\epsilon(\omega) = \epsilon_\infty - \frac{4\pi\tilde{\sigma}(\omega)}{i\omega} \equiv \epsilon_\infty - \frac{\omega_p^2(\omega)}{i\omega(\gamma(\omega) - i\omega)}, \quad (1)$$

where  $\epsilon_\infty$  is the high-energy dielectric constant, which is a high-energy contribution of the interband transitions,  $\tilde{\sigma}(\omega)$  is the complex conductivity,  $\gamma(\omega)$  is the energy-dependent scattering rate, and  $\omega_p(\omega)$  is the plasma frequency. The plasma frequency  $\omega_p(\omega)$  is defined as

$$\omega_p^2(\omega) \equiv \frac{4\pi n e^2}{m^*(\omega)},$$

where  $n$  is the total density of conduction electrons, and  $m^*(\omega)$  is the energy-dependent effective mass.

To begin, let us confine our attention to the plasma frequency. If we assume that the nominal electron number per vanadium ion is exactly 1 for the whole composition range, we can deduce the carrier density  $n$  from the unit-cell volume. Then, we can estimate a variation of the effective mass  $m^*(\omega)$  from the value of  $\omega_p(\omega)$ .

The Energy-loss function  $\text{Im}(-1/\epsilon)$  is obtained by the Kramers-Kronig analysis of the measured reflectivity spectra  $R(\omega)$ . Provided that  $\gamma(\omega)$  and  $m^*(\omega)$  do not depend on  $\omega$  strongly, we can estimate  $\omega_p(= \text{const.})$  from the Energy-loss function, because, the Energy-loss function peaks at the energy of  $\omega_p^*$  ( $\omega_p^* = \omega_p/\sqrt{\epsilon_\infty}$ ). Accordingly, we can obtain the energy-independent plasma frequency  $\omega_p$  from the peak position of the energy-loss function.

In Fig. 4, the spectra of  $\text{Im}(-1/\epsilon)$  of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  are shown in the photon energy range from 0.6 to 2.0 eV

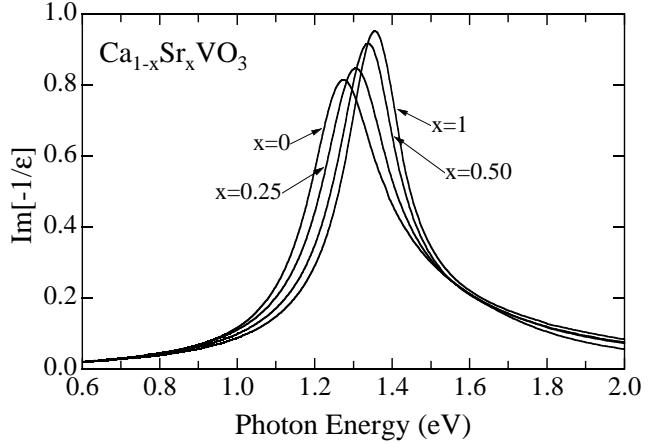


FIG. 4. Energy-loss function  $\text{Im}[-1/\epsilon(\omega)]$  obtained by the Kramers-Kronig transformation of the reflectivity data. The data in the photon energy range between 0.6 eV and 2.0 eV are shown to focus on the plasmon peak (around 1.3 eV).

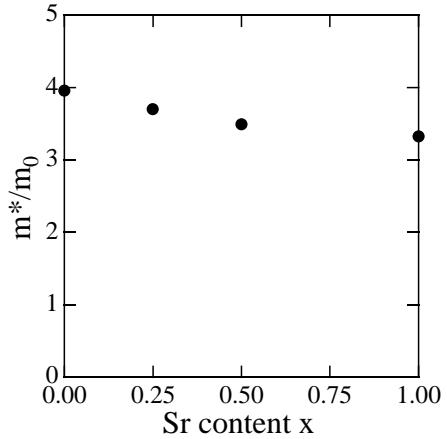


FIG. 5. Effective mass  $m^*$  estimated by the plasma frequencies compared with the bare electron mass  $m_0$ . The value of  $m^*/m_0$  systematically increases in going from  $\text{SrVO}_3$  ( $x = 1$ ) to  $\text{CaVO}_3$  ( $x = 0$ ).

to focus on the peak near the reflectivity edge (around 1.3 eV). The peak position of the Energy-loss function  $\omega_p^*$  systematically shifts to higher energy with increasing  $x$ . At first, we have estimated  $\omega_p^*$  from the peak energy, and deduced  $\omega_p = \sqrt{\epsilon_\infty}\omega_p^*$ . If we consider only the response of the conduction electrons,  $\epsilon_\infty$  is the contribution from the high-energy interband transitions. Since the interband transition appeared above  $\sim 2.5$  eV, the value of  $\epsilon_\infty$  can be taken from the real part of the dielectric function  $\epsilon_1(\omega)$  at around 2.5 eV.<sup>22</sup> Since the value of  $\epsilon_1(\omega \sim 2.5\text{eV})$  is nearly independent of  $x$ , we have used  $\epsilon_\infty = 4$  over the whole composition range. Then, we can deduce the value of  $m^*$  using the lattice constants and the value of  $\omega_p$ .

In Fig. 5, the ratios of the deduced effective mass  $m^*$  to the bare electron mass  $m_0$  are plotted as a function of the Sr content  $x$ . The value of  $m^*/m_0$  systematically increases as varying  $x$  from  $\text{SrVO}_3$  to  $\text{CaVO}_3$ . This carrier-mass enhancement, however, is not so large, even though the system is near the Mott transition. This result is con-

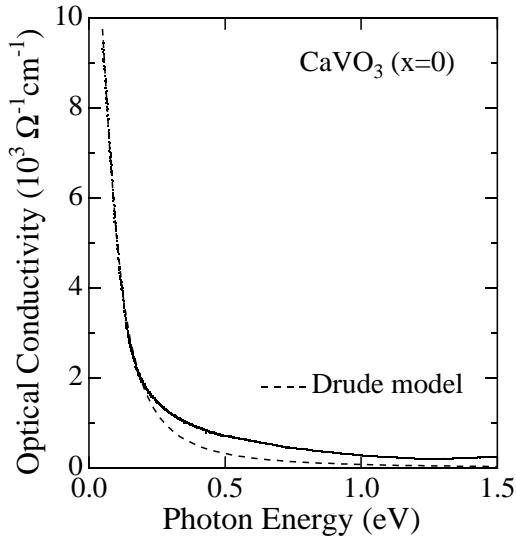


FIG. 6. Comparison between the optical conductivity calculated by the simple Drude model and that of the experiment of  $\text{CaVO}_3$ .

sistent with the value of  $m^*$  estimated from the results of the specific heat measurements.<sup>14</sup>

It is instructive to compare the measured low frequency  $\tilde{\sigma}(\omega)$  with the simple Drude model, in which  $\gamma(\omega)$  and  $m^*(\omega)$  do not depend on  $\omega$ . According to Eq. (1), the real part of the optical conductivity  $\text{Re}[\tilde{\sigma}(\omega)] \equiv \sigma(\omega)$  is given by the formula

$$\sigma(\omega) = \frac{\sigma_{dc}}{1 + \omega^2/\gamma^2},$$

where  $\sigma_{dc}$  is the dc conductivity. The dc conductivity is expressed by the scattering rate  $\gamma$  and the plasma frequency  $\omega_p$  by the following relation:

$$\sigma_{dc} = \frac{ne^2}{m^*\gamma} = \frac{\omega_p^2}{4\pi\gamma}.$$

Here, we have used the value of  $\sigma_{dc}$  obtained by electric resistivity measurements at room temperature. Then the value of  $\gamma$  can be deduced from the above relation. Fig. 6 shows the comparison of the experimentally obtained  $\sigma(\omega)$  for  $\text{CaVO}_3$  to the optical conductivity calculated by the simple Drude model. As shown in Fig. 6, the contribution to the optical conductivity below  $\sim 1$  eV, which is considered to be a response of the itinerant carriers, is not properly reproduced with the simple Drude model especially above 0.2 eV. As we increase the photon energy, the experimentally obtained  $\sigma(\omega)$  deviates from that of the simple Drude model. The observed  $\sigma(\omega)$  has a tail decaying slower than the Drude-type  $\omega^{-2}$  dependence.

We consider that the discrepancy between the simple Drude model and the experimental results is attributed to the energy-dependence of the scattering rate  $\gamma(\omega)$  and the effective mass  $m^*(\omega)$ . The  $\gamma(\omega)$  corresponds to the renormalized scattering rate  $\tau^{*-1}(\omega)$ , which is  $\tau^{-1} \times (m/m^*(\omega))$ . The quantity  $\tau(\omega)$  is closer to the

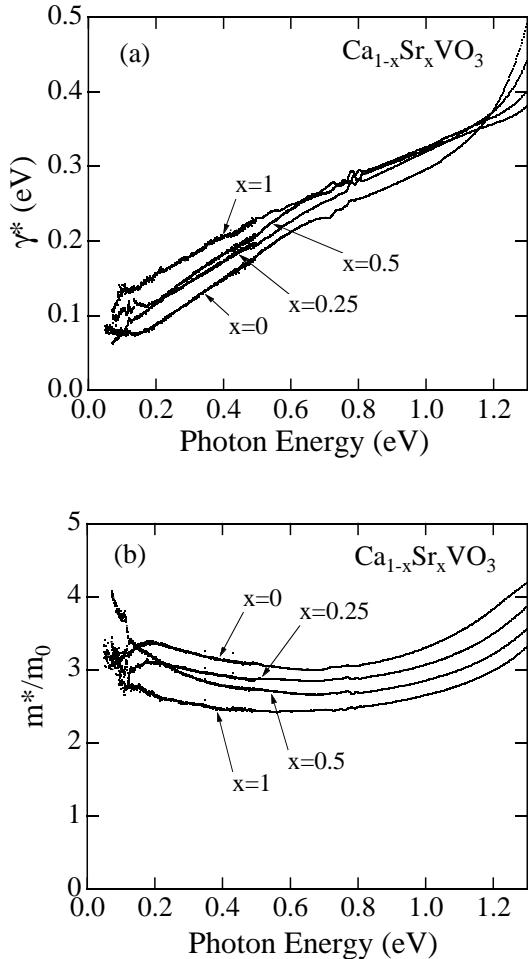


FIG. 7. (a) Energy dependent scattering rates  $\gamma(\omega)$  of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ ; (b) effective mass  $m^*(\omega)$  of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ .  $m^*(\omega)$  is normalized to the bare electron mass  $m_0$ .

microscopic intrinsic quasiparticle lifetime at  $T = 0$ . We can determine  $\gamma(\omega)$  and  $m^*(\omega)$  from Eq. (1); *i.e.*, when we define  $\epsilon(\omega) \equiv \epsilon_1(\omega) + i\epsilon_2(\omega)$ ,

$$\gamma(\omega) = \frac{\omega\epsilon_2(\omega)}{\epsilon_\infty - \epsilon_1(\omega)},$$

$$\begin{aligned} m^*(\omega) &= \frac{4\pi ne^2}{\omega^2} \text{Re} \left[ \frac{1}{\epsilon_\infty - \epsilon(\omega)} \right] \\ &= \frac{4\pi ne^2}{\omega^2} \frac{\epsilon_\infty - \epsilon_1(\omega)}{(\epsilon_\infty - \epsilon_1(\omega))^2 + \epsilon_2^2(\omega)}. \end{aligned}$$

Figs. 7(a) and 7(b) show  $\gamma(\omega)$  and  $m^*(\omega)$  of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  as a function of photon energy. In case of the simple Drude model, the scattering rate  $\gamma$  is provided to be independent on the photon energy. But, in this system,  $\gamma(\omega)$  actually increases as we increase the photon energy, as shown in Fig. 7(a).

The energy-dependent scattering rate is generally based on the electron-phonon scattering and the electron-electron scattering. Since an extremely large  $T^2$ -dependence of the dc conductivity observed in the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system can be well ascribed to the

electron-electron scattering,<sup>14</sup> it is reasonable to consider that the electron-electron scattering governs the behavior of  $\gamma(\omega)$ . According to the Fermi liquid theory, the electron-electron scattering rate is proportional to  $\omega^2$ . Fig. 7(a), however, indicates that  $\gamma(\omega)$  looks more proportional to  $\omega$  rather than  $\omega^2$ . On the contrary, since the electron-phonon scattering is proportional to  $\omega^5$  up to the Debye frequency, it is necessary to elucidate the scattering process which contributes to  $\gamma(\omega)$ . This is still an open question.

On the other hand, the energy dependence of  $m^*(\omega)$  is not so large. Except for the low energy region ( $\omega < \sim 0.2$  eV), the value of  $m^*/m_0$  increases with the decrease of Sr content  $x$ . In the  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$  system, which is a typical doping system, as one approaches  $x = 1$ , a large energy dependence of  $m^*$  as well as a critical enhancement at the low-energy region are observed.<sup>2</sup> However, in  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system,  $m^*$  does not exhibit such a critical enhancement with varying  $x$  in going from  $\text{SrVO}_3$  to  $\text{CaVO}_3$ , although there is a difference between the filling control and the band-width control.

In the low energy limit ( $\omega = 0$ ),  $m^*$  should correspond to the effective mass estimated by the specific heat measurement. We have interpolated  $m^*(\omega)$  down to  $\omega = 0$  with two kinds of tangential lines drawn from 0.4 eV and 0.15 eV. As shown in Fig. 8(a), the intercepts, at which the two tangential lines from 0.4 eV and 0.15 eV cut the vertical axis, are defined as  $m_a$  and  $m_b$ . Fig. 8(b) indicates  $x$ -dependence of the values of  $m_a$  and  $m_b$ . The value of  $m_b$  does not show a systematic behavior, because phonons, randomness, or other extrinsic contributions possibly cause this non-systematic change. However, the value of  $m_a$  increases systematically with decreasing  $x$ ; moreover, the values are almost equal to the value of  $m^*$  deduced from plasma frequency. We regard  $m_a$  as a good measure of  $m^*/m_0$  for this system.

The effective mass estimated from the plasma frequencies and the generalized Drude analysis ( $m_a$ ) appear in Table I. It is expected that we should observe, near the Mott transition, a critical enhancement of the effective mass of the  $3d$  conduction electrons. If we substitute the  $\text{Ca}^{2+}$  ion for the  $\text{Sr}^{2+}$  ion in the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system, the  $3d$  band-width successively decreases. Then, the value of  $m^*/m_0$  is expected to increase drastically reflecting the change of the  $U/W$  ratio. But we have observed that such a large mass enhancement does not actually take place in this system. This is consistent with the result shown in the preceding paper.<sup>14</sup>

TABLE I. Effective mass  $m^*/m_0$  deduced from the plasma frequencies  $\omega_p$  and the generalized Drude model ( $m_a$ ).

$x$	0	0.25	0.5	1
$m^*/m_0$ (deduced from $\omega_p$ )	3.9	3.7	3.5	3.3
$m_a$ (generalized Drude analysis)	3.5	3.2	3.1	2.7

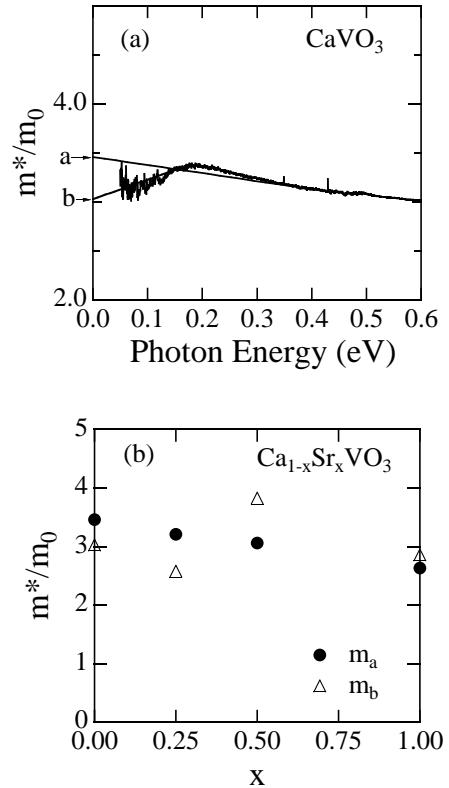


FIG. 8. (a) Energy dependent effective mass  $m^*(\omega)$  of  $\text{CaVO}_3$  compared with the bare electron mass. “a” and “b” indicate intercepts at which tangential lines drawn from 0.4 eV and 0.15 eV cut the vertical axis, corresponding to the values of  $m_a$  and  $m_b$ . (b)  $m_a$  and  $m_b$  are plotted against the Sr content  $x$ .

### C. Spectral weight redistribution of $3d$ -band

The density of states (DOS) of orthorhombic  $\text{CaVO}_3$  and cubic  $\text{SrVO}_3$  calculated using the full-potential augmented plane-wave method with the local density approximation (LDA) are shown in the top of Fig. 9. The band-calculation shows that the DOS near the Fermi level  $E_F$  is dominated by the V  $3d$  electrons. The V  $3d$  band crosses the Fermi level, and the DOS below 4 eV is mainly the O  $2p$  band.

In the metallic states,  $\sigma(\omega)$  is expected to consist of two basic components: intraband transitions within the V  $3d$  conduction band, *i.e.*, the Drude part extending from  $\omega = 0$ , and interband transitions appearing at much higher energy. The latter is regarded from the calculated DOS as the charge-transfer contribution (an excitation from the O  $2p$  band to the unoccupied part of the V  $3d$  band above  $E_F$ ). A corresponding schematic picture of the optical conductivity is shown in the bottom of Fig. 9. As seen in the picture, the charge-transfer contribution is expected to appear above  $\sim 4$  eV, and the absorption edge of the charge-transfer transition in  $\text{SrVO}_3$  is considered to shift slightly to lower energy than that of  $\text{CaVO}_3$ , reflecting the shift of the O  $2p$  band.

Based on this picture, let us now look at the experimental results, Fig. 10 shows the real part of the optical conductivity,  $\sigma(\omega)$ , of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  single crystals

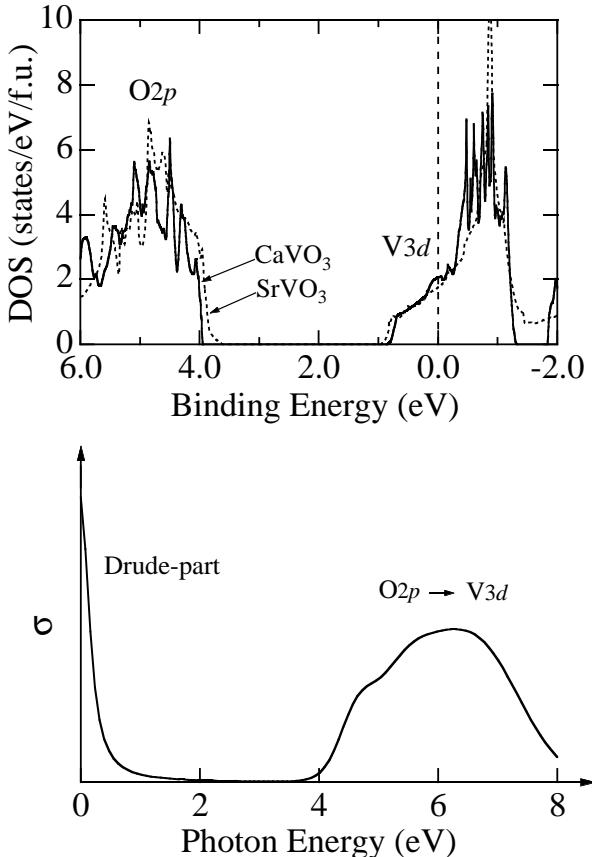


FIG. 9. DOS of CaVO<sub>3</sub> and SrVO<sub>3</sub> obtained by the LDA band calculation (top) and a schematic picture of optical conductivity expected from the calculated DOS (bottom).

( $x=0, 0.25, 0.50, 1$ ). The optical conductivity spectra are different from our naive schematic picture (Fig. 9 bottom); they show the presence of two anomalous features in the intraband transition part below 4 eV besides the Drude-like absorption (discussed above): a small peak which appears at  $\sim 1.7$  eV and a large peak at  $\sim 3.5$  eV. It must be noted that the two peak-like structures below 4 eV have no naive origin as far as we can infer from the calculated DOS (Fig. 9). This large spectral weight redistribution is generally believed to be a manifestation of the strong electron correlation in this system.

Fig. 11 shows a comparison of the optical conductivity spectra of CaVO<sub>3</sub> to those of other perovskite oxides, Sr<sub>0.95</sub>La<sub>0.05</sub>TiO<sub>3</sub> (lightly doped 3d<sup>0.05</sup> metal),<sup>23</sup> and YTiO<sub>3</sub> (3d<sup>1</sup> insulator) reported by Okimoto *et al.*<sup>8</sup> In the optical conductivity of Sr<sub>0.95</sub>La<sub>0.05</sub>TiO<sub>3</sub>, the most prominent low-energy feature, that distinctly rises around 4 eV, can be interpreted as originating in a transition from the O 2p band to the Ti 3d band, which corresponds to the optical gap of the parent insulator SrTiO<sub>3</sub>.<sup>24</sup> The doped 3d electrons contribute to  $\sigma(\omega)$  with a small spectral weight extending from  $\omega = 0$ . On the other hand, YTiO<sub>3</sub> is considered to be a Mott-Hubbard insulator. Two electronic gap-like features are observed around 1 eV and 4 eV. These features have been respectively interpreted as originating in excitations through the Mott-Hubbard

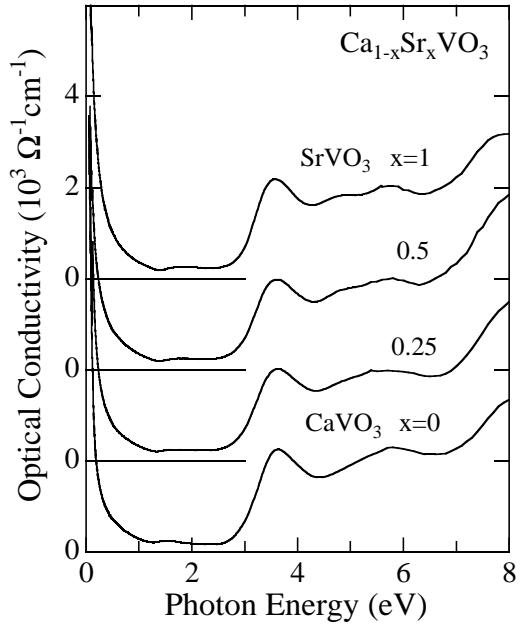


FIG. 10. Optical conductivity spectra of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  single crystals ( $x=0, 0.25, 0.50, 1$ ) at room temperature obtained by the Kramers-Kronig transformation of the reflectivity data.

gap, namely, from the lower-Hubbard band (LHB) to the upper-Hubbard band (UHB), and an excitations through the charge-transfer gap, *i.e.*, from the O 2p band to the UHB.<sup>8,25</sup> Recently, Bouarab *et al.* have reported interband optical conductivities obtained by the energy-bands calculation of the  $\text{YMO}_3$  ( $M=\text{Ti-Cu}$ ) system with a local spin-density approximation.<sup>26</sup> Their calculated results of interband optical conductivity in YTiO<sub>3</sub> is shown in the bottom of Fig. 11 as a shaded portion. We find out from this comparison that the peak at around 5 eV cannot be explained by the transition between the O 2p band and the Ti 3d band alone.

In CaVO<sub>3</sub>, photoemission spectroscopy<sup>15,27</sup> has revealed that the O 2p band is located at a binding energy which is almost the same as that of metallic Sr<sub>0.95</sub>La<sub>0.05</sub>TiO<sub>3</sub>; hence, the absorption edge of the charge-transfer excitation of CaVO<sub>3</sub> should be approximately equal to that of Sr<sub>0.95</sub>La<sub>0.05</sub>TiO<sub>3</sub>. Therefore, it is reasonable to consider that the shaded portions of  $\sigma(\omega)$  in Fig. 11 correspond to the charge-transfer type transitions as well as the other interband transitions with much higher energies, on the analogy of the band-calculation in YTiO<sub>3</sub>.<sup>26</sup> Accordingly, the remaining white portions correspond solely to the intraband transition within the V 3d band.

In order to focus on the spectral weight of the optical conductivity arising from intra-3d-band transitions, we have subtracted the shaded portion in the middle of Fig. 11 as backgrounds, assuming an appropriate function of  $(\omega - \Delta)^{3/2}$ , where  $\Delta$  has been obtained by fitting the lower energy tail of the O 2p band in photoemission spectroscopy spectra of  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  single crystals.<sup>28</sup>

A quantitative measure of the spectral weight has been

obtained by deducing the effective electron number per vanadium ion defined by the following relation

$$N_{\text{eff}}(\omega) \equiv \frac{2mV}{\pi e^2} \int_0^\omega \sigma(\omega') d\omega',$$

where  $e$  is the bare electronic charge and  $m$  is the bare band mass of a non interacting Bloch electron in the conduction band.  $V$  is the cell volume for one formula unit (one V atom in this system). The significance of  $N_{\text{eff}}$  will be appreciated by considering the sum rule of the conductivity

$$\int_0^\infty \sigma(\omega) d\omega = \frac{\pi N e^2}{2mV}$$

where  $N \equiv N_{\text{eff}}(\infty)$  corresponds to the total number of electrons in the unit formula. That is,  $N_{\text{eff}}(\omega)$  is proportional to the number of electrons involved in the optical excitations up to  $\omega$ . In Fig. 12, we show  $N_{\text{eff}}$  of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system, after subtracting the higher-energy background. Since, in Fig 12, we have assumed  $m = m_0$ , where  $m_0$  is the bare electronic mass, the total number  $N \equiv N_{\text{eff}}(\omega = \infty) \simeq N_{\text{eff}}(\omega = 5 \text{ eV})$  results smaller than 1, reflecting the difference between  $m$  and  $m_0$  ( $m > m_0$ ). If we rather use the value  $m$  obtained from LDA,  $m \sim 1.5m_0$  for the V 3d band, we find  $N_{\text{eff}}(5 \text{ eV}) \approx 1$ . Thus, we conclude that the assumed background (shaded area in Fig. 11) is reasonable to deduce the intrinsic contributions of the interband transition.

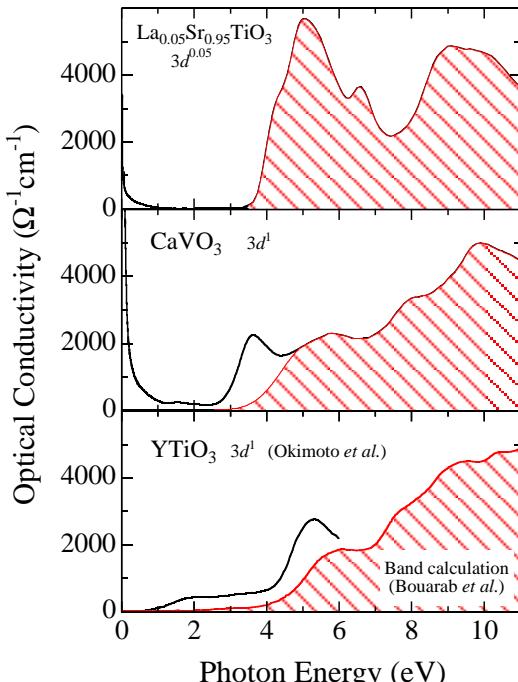


FIG. 11. Comparison of the optical conductivity spectra of  $\text{CaVO}_3$  to those of other perovskite oxides,  $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$  (lightly doped  $3d^0$  metal),<sup>23</sup> and  $\text{YTiO}_3$  ( $3d^1$  insulator) reported by Okimoto *et al.*<sup>8</sup> Shaded portions correspond to the interband transition, and remaining white portions correspond solely to the intraband transitions within the V 3d band.

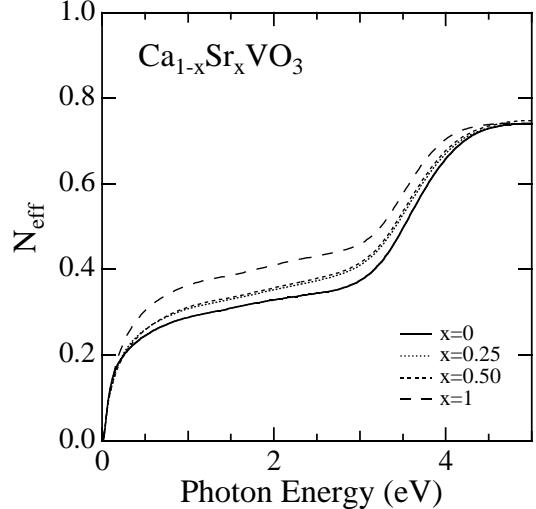


FIG. 12. Effective electron number per vanadium atom  $N_{\text{eff}}$  obtained after subtracting the higher-energy background (Fig. 11).

The initial steep rise of  $N_{\text{eff}}$  is due to the Drude-like contributions extending from  $\omega = 0$ . The Drude-like contribution can be distinguished below  $\sim 1.5$  eV, where  $N_{\text{eff}}$  exhibits a flat region. Therefore,  $N_{\text{eff}}$  at  $\sim 1.5$  eV is considered to be a good measure for the effective mass of the carriers. The values of  $m^*/m_0$  estimated from  $N_{\text{eff}}(\omega = 1.5 \text{ eV})$  are 3.1(6), 3.0(5), 3.0, 2.7 for  $x = 0, 0.25, 0.50, 1$ , which are almost equivalent to the values of  $m^*/m_0$  discussed in Sec. IIIB.

Fig. 13 shows the optical conductivity spectra  $\sigma(\omega)$  of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  single crystals ( $x=0, 0.25, 0.50, 1$ ) in the photon energy range of 0~5 eV. The high-energy background corresponding to the interband transition is subtracted. As discussed above,  $\sigma(\omega)$  ( $0 \leq \omega \leq 5 \text{ eV}$ ) reflects only the intraband transition of the V 3d electrons. In the spectrum, there is a small feature at  $\sim 1.7$  eV, which we call a peak “A” [Fig. 13(a)] and also a large feature at  $\sim 3.5$  eV, which we call a peak “B” [Fig. 13(b)]. With the increase of  $x$ , the excitation energy of the peak “B” shifts slightly to lower energy, and its spectral weight decreases; whereas, the excitation energy of the peak “A” shifts to higher energy, and its spectral weight increases. In addition, the width of the peak “A” broadens with the increase of  $x$ . Fig. 14 shows the excitation energy, the full-width at half maximum (FWHM), and the spectral weight of the peak “A” and the peak “B” as functions of  $x$ .<sup>29</sup>

In the valence band photoemission spectra of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system, two features have been observed: one is a peak at  $\sim 1.5$  eV below  $E_F$  and the other is the emission from a broad quasiparticle band which lies on  $E_F$ .<sup>15,27</sup> The former is assigned to an incoherent emission associated with the formation of the lower Hubbard band and the latter corresponds to a renormalized 3d band at  $E_F$ . Inoue *et al.* reported that, upon increasing the strength of  $U/W$  in  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system, the spectral weight is systematically transferred from the quasi-

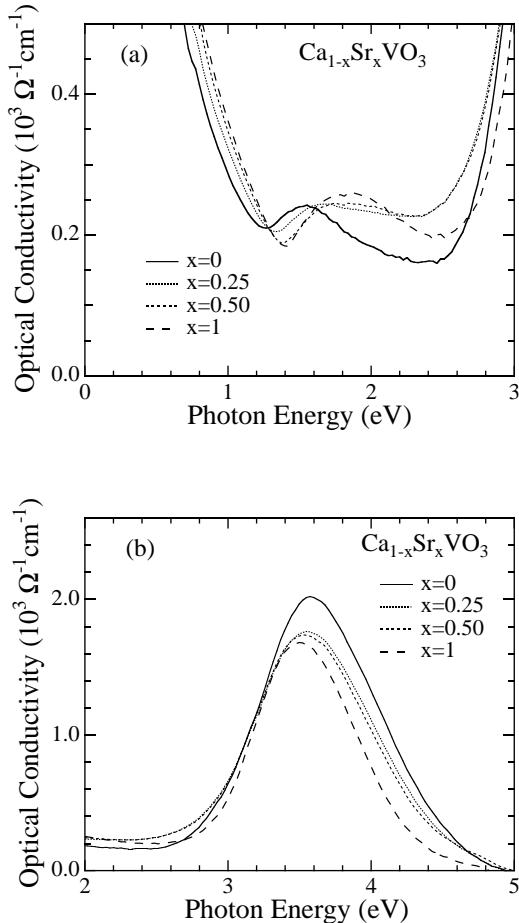


FIG. 13. Optical conductivity spectra of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  in the photon energy range of 0~5 eV. The high-energy background corresponding to the interband transition is subtracted. (a) a small peak at  $\sim 1.7$  eV denoted as peak “A” in the text. (b) a large peak at  $\sim 3.5$  eV denoted as peak “B” in the text.

particle band to the incoherent part.<sup>15</sup> In the inverse-photoemission spectra of  $\text{CaVO}_3$  and  $\text{SrVO}_3$ , Morikawa *et al.* have found a prominent peak at  $2.5\sim 3$  eV above  $E_F$  and a shoulder within around 1 eV of  $E_F$ .<sup>27</sup> These features have been also assigned to the incoherent and coherent parts of the spectral function of the V 3d electron around the Fermi level.

These results lead us into consideration that the two features (the peak “A” and “B”) observed in the optical conductivity spectra should originate in possible combinations of the transitions among the incoherent and coherent features of V 3d electron around the Fermi level.

The experimental results of the optical conductivity can be compared to the theoretical prediction obtained by the self-consistent local-impurity approximation of the infinite-dimension Hubbard model.<sup>12</sup> The theory seems to give us a clue to understand the origin of the two features: the peak “A” and the peak “B”. According to the prediction, the optical response is composed of basically three contributions except the Drude part: a broad part centered at a frequency  $\omega = U$ , a few narrow features

near  $\omega = U/2$ , and an “anomalous” part that is present in the range  $\omega = 0$  to 1 eV approximately. The contribution at  $U$  corresponds to direct excitations between the Hubbard bands, the features at  $U/2$  corresponds to excitations from the LHB to the empty part of the quasiparticle band and from the filled part of the quasiparticle band to the UHB, and finally, the “anomalous” part corresponds to excitations from the filled to the empty part of the quasiparticle band. In our previous paper,<sup>30</sup> we analyzed the spectrum of  $\text{CaVO}_3$  in the light of these predictions. The parameters  $U$  and  $W$ , which were used in the model calculation, were taken from the results of photoemission spectroscopy.<sup>30</sup> Although it was expected that the parameter  $W$  would systematically change with composition, we chose to vary  $U$  for the sake of simplicity,

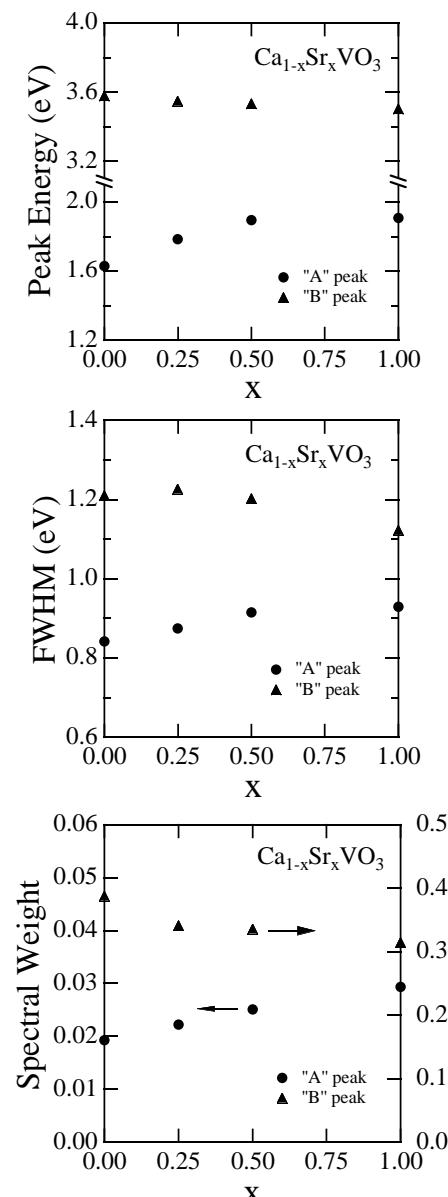


FIG. 14. Excitation energy, full-width at half maximum (FWHM), and spectral weight of the peak “A” and the peak “B” plotted as functions of  $x$ .

given that fits of equivalent quality could be obtained for the photoemission spectra. In  $\text{CaVO}_3$ , which has the narrowest  $3d$  band in the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system, the peaks “A” and “B” have been well described by the features at  $U/2$  and  $U$ , respectively, so that the infinite-dimension Hubbard model seems to reproduce the experimentally obtained optical conductivity reasonably well.<sup>30</sup>

We find that our new experimental results as summarized in Fig. 14: with the increase of  $x$ , the peak energy of the peak “B” shifts slightly to lower energy side and its spectral weight gradually increases. The spectral weight of the peak “A” increases with  $x$ . The peak “A”, however, shifts slightly to higher energy. We shall now like to emphasize an important point. Our present systematic study of the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  compound gives conclusive evidence that we can tune the band-width of the system by controlling  $x$ . The position of the peak “B” gives a direct measure of the value of  $U$ , and the fact that it remains almost a constant is a clear evidence that the ratio  $U/W$  is controlled by a change of the band-width  $W$ . This situation is in sharp contrast with our previous analysis<sup>30</sup> based on photoemission data which did not allow us to resolve which parameter was actually controlling the  $U/W$  ratio. A crucial ingredient that makes the study of the optical response so valuable for this analysis is that, unlike photoemission, it probes also the unoccupied part of the spectra, therefore, it is sensitive to the relative position of the Hubbard bands.

In order to gain some further insight in the qualitative behavior of the systematic evolution of our experimental data, we have used our initial estimates for  $U$  and  $W$  as input parameters in a calculation of the optical response of the Hubbard model and changed the value of  $W$  instead of  $U$ . We shall consider the model within the dynamical mean field theory which becomes exact in the limit of large lattice connectivity (or large dimensionality). For convenience we have computed the optical response using the iterated perturbation theory (IPT) method which allows for a simple evaluation of this quantity at  $T = 0$  and near the Mott-Hubbard transition.<sup>31,32</sup>

In Fig. 15 we show the theoretical prediction using the value of  $U = 3$  eV for the local repulsion and for the half-bandwidth  $W/2 = 1.05$  and  $0.95$  eV for  $\text{SrVO}_3$  and  $\text{CaVO}_3$ , respectively. Note that the spectra do not display the Drude contribution as it corresponds to a delta-function at  $\omega = 0$  since our model does not contain disorder and the calculation is performed at  $T = 0$ . The particular lineshape that we obtain is originated in the behavior of the spectral density of states that is obtained within the IPT method as shown in Fig. 16. We should point out that while the details of the line shape may not be correctly given by this method, the main distribution of the spectral weight of the various contributions and their systematic evolution are very reliably captured.<sup>12</sup>

We observe that the theoretical results for the systematic dependence of the various contributions to the optical response by controlling the value of  $W$  are in a better qualitative agreement with the experimental data of Fig. 14 than the previous calculation where we changed

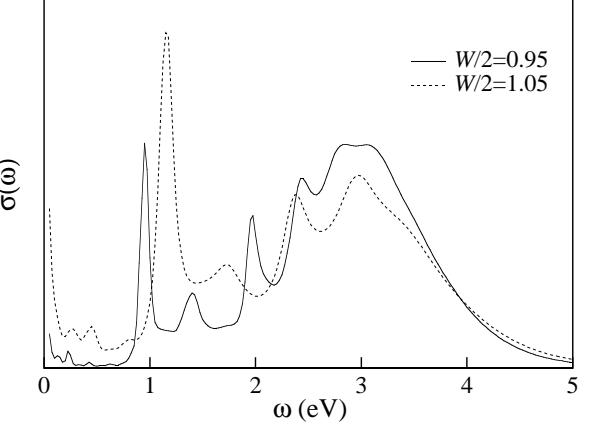


FIG. 15. Calculated optical conductivity by IPT for the parameters  $U = 3$  eV and  $W$  indicated in the figure.

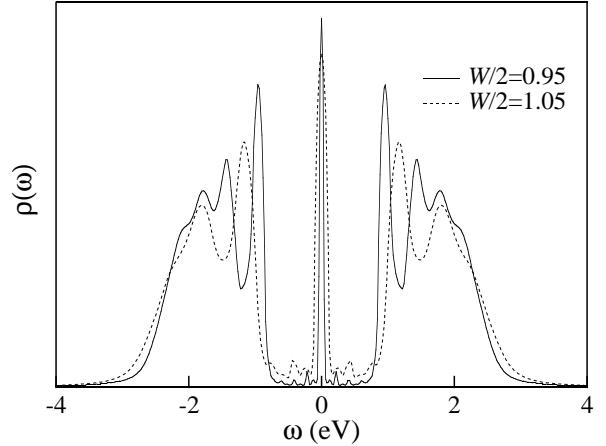


FIG. 16. Theoretical spectral density of states obtained by IPT at  $T = 0$  for the parameters  $U = 3$  eV and  $W$  indicated in the figure.

the value of  $U$ . One of the most notable improvements consists in that the unexpected systematic evolution of the feature at  $U/2$ , which shifts upward with increasing  $W$ , is well qualitatively captured. This peculiar effect can be interpreted as a “band repulsion” between the Hubbard band and the quasiparticle band. As we increase  $W$ , the latter becomes broader and “pushes” the Hubbard band further out.

However, there are still some discrepancies. Such a large spectral weight redistribution is predicted to be concomitant with a large effective mass in the mean-field treatment of the Hubbard model.<sup>12,33</sup> This is, however, inconsistent with the observed effective mass in this system. Moreover, in the optical conductivity spectra, there is apparently a notable discrepancy in respect to the relative spectral weight of the peak “A” to the peak “B”. It is remarkably suppressed in the experimental data, compared with the theoretical data.

Other discrepancies between some experimental results and the prediction of the mean-field approach for the electron correlation were also reported in the photoemission spectroscopy measurements in this system.<sup>15,27</sup>

In the mean-field Fermi liquid approach, the renormalized quasiparticle band at  $E_F$  should be narrowed with increasing the value of  $U/W$ ,<sup>12,33</sup> but, in those experiments, the quasiparticle band-width remains broad, even if the system approaches to the Mott transition. Since the peak “A” has been assigned to the transitions associated with the quasiparticle band, the conspicuous suppression in spectral intensity of the peak “A” reflects the broadness of the quasiparticle band. The broad quasiparticle band also accounts for the lack of the strong mass enhancement in this system.

As discussed in the preceding paper,<sup>14</sup> the momentum-dependent self-energy becomes significant near the Mott transition, resulting in a reduction of the mass enhancement. Although our measurement cannot clarify the validity of introducing a momentum-dependent self-energy, we conclude that there must be other interactions not present in the mean-field treatment of the electron correlation in the metallic regime close to the Mott transition.

Finally, the presence of the “anomalous” contribution at low frequencies that extends down to  $\omega = 0$  in the theoretical data sheds a different light for the interpretation of the Drude-like response discussed in Sec. IIIB. It may be possible to say that the deviation from the simple Drude model would be partly due to this “anomalous” contribution. The origin of this effect is again traced to the presence of the incoherent contribution coming from the low energy tails of the Hubbard bands that is observed in the theoretical density of states. However, it is experimentally very difficult to disentangle unambiguously the contribution of the coherent optical response of carriers and that of the incoherent process in optical conductivity, so this issue remains an open question.

#### IV. CONCLUSIONS

This study has aimed at elucidating the electronic structure of the correlated metallic vanadate by means of the optical spectroscopy measurements. We have synthesized the  $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$  system to control solely the  $3d$  band-width without varying the band filling.

We have found that the low energy contribution to the optical conductivity spectra cannot be reproduced by the simple Drude model with the energy-independent scattering rate and effective mass. The energy-dependent  $\gamma(\omega)$  determined by the generalized Drude model shows relatively large energy dependence. However,  $\gamma(\omega)$  is proportional to  $\omega$  rather than that of the electron-electron scattering  $\omega^2$ .

The effective mass of the V  $3d$  electron has been evaluated from the plasma frequency. The value of  $m^*/m_0$  gradually increases with decreasing the band-width  $W$ . However, any symptom of the critical mass enhancement has not been observed, even though the system is close to the Mott transition.

We observed two anomalous peaks in the optical conductivity spectra around 1.7 eV and 3.5 eV. These features can be assigned to the possible combinations of transitions between the incoherent and coherent bands of quasiparticles around the Fermi level. This large spectral weight redistribution substantiates the strong electron correlation in this system, which is, however, not concomitant with a large effective-mass enhancement.

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